Thermodynamically Consistent and Meta-Stable Equation of State Models for Hydro and Solid Dynamics

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Basic Euler Equations for Material Separated Flows

- This model, which is commonly assumed in front tracking contexts, assumes there is no mixing in a fluid volume and that different materials are separated by resolved interfaces
- The flow equations in this case are identical to the single component Euler equations:

$$\frac{\partial \rho}{\partial t} + \nabla \bullet (\rho \mathbf{u}) = 0$$

$$\frac{\partial \rho \mathbf{u}}{\partial t} + \nabla \bullet (\rho \mathbf{u} \otimes \mathbf{u}) + \nabla P = 0$$

$$\frac{\partial \rho \left(\frac{1}{2}u^2 + e\right)}{\partial t} + \nabla \bullet \left[\rho \mathbf{u}\left(\frac{1}{2}u^2 + e\right) + P\mathbf{u}\right] = 0$$

  – For simplicity we assume rectangular geometry and no sources

The Equation of State (EOS)

- The basic conservation laws of mass, momentum, and energy are not sufficient to define a flow.
- The additional information for closure of this system is provided by the Equation of State that describes the relation between the material thermodynamic variables, including
  - Mass Density, *ρ*, Specific volume, $V = 1/\rho$, Pressure, *P*, Specific internal energy, *e*, Temperature, *T*, Specific Entropy, S
  - Specific Free Energies
    - Specific internal energy, *E*, Specific Helmholtz free energy, *F*
    - Specific enthalpy, *H*, Specific Gibb's free energy, *G*
- Generally the equation of state is accessed through one of the following representations
  - Incomplete equation of state $P = P(\rho,e)$
    - Does not define a temperature
    - It is not uncommon to define an ad-hoc inconsistent temperature such as $e = C_V T + e_0$
  - A complete equation of state is needed to define a consistent temperature
    - $e = e(V,S)$, $de = TdS - PdV$, $F = F(V,T)$, $dF = -SdT - PdV$
    - $H = H(P,S)$, $dH = TdS + VdP$, $G = G(P,T)$, $dG = -SdT + VdP$
  - The free energy forms of the equation of state are equivalent in a certain sense and can be derived from one another via Legendre transformations
  - An incomplete equation of state can be derived from a complete equation of state but not vice versa

What Does the Equation of State Mean in a Practical Sense?

- The basic conservation laws are completely abstract and universal. Thus they apply to everything, but specify nothing about a particular material.
- Flows have considerable differences depending on the nature of application
  - Physical phase
    - Gas, relatively low density, low sound speed
    - Liquids, high densities, high sound speed
    - Solids, high densities, high sound speed
      - Plus usually connected to additional equations that describe the material strength, such as elastic and plastic properties.

Thermodynamic Stability

- The free energies are also constrained by thermodynamic stability to satisfy certain convexity restrictions
  - e(V,S) is a convex function of specific volume and specific entropy
  - G(P,T) is a concave function of pressure and temperature
  - F(V,T) is convex in specific volume and concave in temperature
  - H(P,S) is concave in pressure and convex in specific entropy
- The free energies can be recovered from one another by Legendre transformation, e.g.

$$F(V,T)=\inf_{S}\left[e(V,S)-TS\right],\ G(P,T)=\inf_{V,S}\left[e(V,S)-TS+PV\right],\ H(P,S)=\inf_{V}\left[e(V,S)+PV\right]$$

$$e(V,S)=\sup_{T}\left[F(V,T)-TS\right],\ G(P,T)=\inf_{V}\left[F(V,T)+PV\right],\ H(P,S)=\inf_{V}\sup_{T}\left[F(V,T)-TS+PV\right]$$

$$e(V,S)=\sup_{T,P}\left[G(P,T)-TS+PV\right],\ F(V,T)=\sup_{P}\left[G(P,T)+PV\right],\ H(P,S)=\sup_{P}\left[G(P,T)-TS\right]$$

$$e(V,S)=\sup_{P}\left[H(P,S)-PV\right],\ F(V,T)=\sup_{P}\inf_{S}\left[H(P,S)-PV-TS\right],\ G(P,T)=\inf_{S}\left[H(P,T)-TS\right]$$

- The invertibility of the free energies via the Legendre transforms is a consequence of their convexity properties
- Most applications will assume the equation of state is smooth, in which case the convexity constraints are in terms of inequalities on the free energy second derivatives:

$$\frac{\partial^2 e}{\partial V^2}\geq 0,\ \frac{\partial^2 e}{\partial S^2}\geq 0,\ \frac{\partial^2 e}{\partial V^2}\frac{\partial^2 e}{\partial S^2}\geq\left(\frac{\partial^2 e}{\partial V\,\partial S}\right)^2,\ \frac{\partial^2 G}{\partial P^2}\leq 0,\ \frac{\partial^2 G}{\partial T^2}\leq 0,\ \frac{\partial^2 G}{\partial P^2}\frac{\partial^2 G}{\partial T^2}\geq\left(\frac{\partial^2 G}{\partial P\,\partial T}\right)^2,\ \frac{\partial^2 F}{\partial V^2}\geq 0,\ \frac{\partial^2 F}{\partial T^2}\leq 0,\ \frac{\partial^2 H}{\partial P^2}\leq 0,\ \frac{\partial^2 H}{\partial S^2}\geq 0$$

Thermodynamic Stability

- Hydrodynamic solvers use a number of quantities that are obtained from derivatives of the free energies
  - Isentropic bulk modulus: $\rho c^2 = -\left.\frac{\partial P}{\partial \log V}\right|_S$
  - Isothermal bulk modulus: $\rho c_T^2 = -\left.\frac{\partial P}{\partial \log V}\right|_T$
  - Grüneisen exponent: $\Gamma = -\left.\frac{\partial \log T}{\partial \log V}\right|_S = V\left.\frac{\partial P}{\partial e}\right|_V$
  - Specific heats at constant volume/pressure:

$$C_V = T\left.\frac{\partial S}{\partial T}\right|_V = \left.\frac{\partial e}{\partial T}\right|_V,\ C_P = T\left.\frac{\partial S}{\partial T}\right|_P = \left.\frac{\partial H}{\partial T}\right|_P$$

  - Stability implies the inequalities:

$$C_P \geq C_V \geq 0,\ \rho c^2 \geq \rho c_T^2 \geq 0,\ \text{in fact } C_P = C_V \frac{\rho c^2}{\rho c_T^2},\ \rho c^2 = \rho c_T^2 + \rho \Gamma^2 C_V T$$

Types of Equations of State

- From a computational point of view, many popular equations of state models fall in one of three classes
  - Simple analytic
    - Gamma Law, Stiff Gamma Law: $P=(\gamma-1)\rho e,\ P+\gamma P_\infty=(\gamma-1)\rho e$
    - Mie-Grüneisen Form: $P-P_r(V)=\frac{\Gamma(V)}{V}\left[e-e_r(V)\right]$
  - Tabular Equations of state where the thermodynamic relations are based on interpolation off discrete values
    - E.g. Los Alamos SESAME EOS: $P_{ij}=P(\rho_i,T_j),\ e_{ij}=e(\rho_i,T_j)$
    - In principle tabular equation of states allow a hydro application to use very general EOS models that have been implemented as a “black box” to the code
      - In practice maybe “not so much a black box”

Complete EOS vs Incomplete

- In cases where an incomplete equation of state is given, a complete equation of state and the corresponding temperature can be computed by solving the partial differential equation:

$$TdS = de + PdV$$

$$dS = \frac{1}{T}de + \frac{P(V,e)}{T}dV \Rightarrow \frac{\partial}{\partial V}\left(\frac{1}{T}\right) = \frac{\partial}{\partial e}\left(\frac{P}{T}\right)$$

$$\frac{\partial T}{\partial V} - P(V,e)\frac{\partial T}{\partial e} = -T\frac{\partial P}{\partial e}$$

- We note that this is a hyperbolic scalar equation for temperature as function of specific volume and specific internal energy, the characteristics of which are the isentropic curves for the incomplete equation of state:

$$\frac{de}{dV} = -P(V,e)$$

- A complete equation of state can be derived by defining temperature data on any non-characteristic curve in specific volume and specific internal energy space. This is commonly done by specifying either temperature direction, or the specific heat at constant volume:

$$C_V = \left.\frac{\partial e}{\partial T}\right|_V$$

Constant Specific Heat

- It can be shown that the specific heat at constant volume and the Grüneisen exponent are related by the equation:

$$\left.\frac{d\log C_V}{d\log V}\right|_S = \left.\frac{d\Gamma}{d\log T}\right|_V$$

- This equation implies that the Grüneisen exponent is a function of volume only, then the specific heat at constant volume is a function of specific entropy only. Thus for the case of a constant C_V the EOS is of the Grüneisen form:

$$P - P_r(V) = \frac{\Gamma(V)}{V}\left[e - e_r(V)\right]$$

- For a constant C_V = de/dT at constant V, the temperature is of the form:

$$e - e_r(V) = C_V\left[T - T_r(V)\right]$$

- Using the PDE for temperature on the previous slide we can show that the reference temperature satisfies the linear differential equation:

$$C_V\left[\frac{dT_r}{dV} + \frac{\Gamma}{V}T_r\right] = P_r(V) + e_r'(V)$$

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Multiple Material Mixtures

- The compressible Euler equations express the basic conservation laws of mass, momentum, and energy
- For a multiple material mixture with no chemical reactions the mass of each component is conserved
- Depending on the choice of flow model the components may be in one of several types of equilibrium
  - Pressure, all materials in a cell are at the same pressure
  - Temperature, all materials in a cell are at the same temperature
  - Velocity, all materials in a cell have a common velocity
- A popular mixture model is to assume all three
  - Imposes a variety of physical restrictions

Separated component pressure/ temperature equilibrium

- A the subgrid level the materials in the mixture are assumed to be separated by interfaces and in pressure/temperature/velocity equilibrium, the basic EOS data is to assume the total specific volume, total specific internal energy, and component mass fractions are known and to solve for the pressure and temperature of the mixture using the assumption that the total internal energy and specific volume is the mass average of the component values leading to systems of the form:

$$e = \sum_{k=1}^{N} \mu_k e_k\left(P,T\right),\ V = \sum_{k=1}^{N} \mu_k V_k\left(P,T\right),\ \text{2 equations in 2 unknowns, Gibb's Free energy form}$$

$$e = \sum_{k=1}^{N} \mu_k e_k\left(V_k,T\right),\ V = \sum_{k=1}^{N} \mu_k V_k,\ P = P_k\left(V_k,T\right),\ k = 1,\cdots,N,\ \text{N+2 equations in N+2 unknowns, Helmholtz Free energy form}$$

$$e = \sum_{k=1}^{N} \mu_k e_k\left(P,S_k\right),\ V = \sum_{k=1}^{N} \mu_k V_k\left(P,S_k\right),\ T = T_k\left(P,S_k\right),\ k = 1,\cdots,N,\ \text{N+2 equations in N+2 unknowns, Enthalpy Free energy form}$$

$$e == \sum_{k=1}^{N} \mu_k e_k\left(V_k,S_k\right),\ V == \sum_{k=1}^{N} \mu_k V_k\ ,P = P_k\left(V_k,S_k\right), T = T_k\left(V_k,S_k\right),\ k = 1,\cdots,N,\ \text{2N+2 equations in 2N+2 unknowns, Internal Free energy form}$$

- The Gibb’s free energy form is the mathematical simplest, but since the energy and density can be discontinuous as functions of pressure and temperature across phase changes the solution may not numerically stable.

Molecular (Dalton) Mix

- In this model, suitable for gas mixtures, the component materials in a mixed cell are assumed to all occupy the same volume, given the total specific internal energy, total specific volume, and mass fractions the equations become:

$\mu_k V_k = V,\ 1 = \sum_{k=1}^{N} \mu_k \Rightarrow$ Component specific volumes are known

$e = \sum_{k=1}^{N} \mu_k e_k\left(V_k, T\right),\ P = \sum_{k=1}^{N} P_k\left(V_k, T\right),$ 1 equation in 1 unknown, Helmholtz free energy form

$e = \sum_{k=1}^{N} \mu_k e_k\left(P_k, T\right),\ V_k = V_k\left(P_k, T\right),\ P = \sum_{k=1}^{N} P_k\left(P_k, T\right),$ N+1 equation in N+1 unknowns, Gibb's free energy form

$e = \sum_{k=1}^{N} \mu_k e_k\left(P_k, S_k\right),\ V_k = V_k\left(P_k, S_k\right),\ T = T_k\left(P_k, S_k\right),\ P = \sum_{k=1}^{N} P_k,$ 2N+1 equation in 2N+1 unknowns, Enthalpy free energy form

$e = \sum_{k=1}^{N} \mu_k e_k\left(V_k, S_k\right),\ T = T_k\left(V_k, S_k\right),\ P = \sum_{k=1}^{N} P_k\left(V_k, S_k\right),$ N+1 equation in N+1 unknowns, Internal free energy form

- Here the total pressure is the sum of the partial pressures of the components

Example: Perfect Gases

- Component EOS: $P_k V_k = (\gamma_k - 1) e_k,\ e_k = C_{V,k} T_k$
- PTE solution: $e = C_V T,\ PV = (\gamma - 1) e,\ C_V = \sum_{k=1}^{N} \mu_k C_{V,k},\ (\gamma - 1) = \frac{1}{C_V} \sum_{k=1}^{N} \mu_k (\gamma_k - 1) C_{V,k}$
- Dalton solution:

$$e = C_V T,\ PV = (\gamma - 1) e,\ C_V = \sum_{k=1}^{N} \mu_k C_{V,k},\ (\gamma - 1) = \frac{1}{C_V} \sum_{k=1}^{N} \mu_k (\gamma_k - 1) C_{V,k},\ P_k V = \mu_k (\gamma_k - 1) C_{V,k} T$$

- For perfect gases the two mixture laws give the same component temperature and pressure. This is a cause of great confusion since the equivalence is not the case for general EOS mixtures.

Front Tracking and Mixtures

- Mixed cell EOS evaluations are not needed for tracked interface if the interfaces separate all of the material components, e.g.
  - FronTier (explicit tracking)
  - Ghost Fluid Level Set
- However problems with diffusion will generally want to use a Dalton type mixture for the resulting cells.
- Problems where only a subset of material interfaces are tracked will likely need either the PTE or Dalton approximate as appropriate.
  - For example at late time where the flow has become highly mixed it may be impractical to track highly convoluted interfaces

PTE Root Finder

- The Gibb's free energy form of the PTE equation is conceptually easy and is essentially an EOS inversion from an pressure/temperature form to an energy/density from
  - Here I will use specific volume and density as more or less interchangeable since on one is the reciprocal of the other
- Given V and e, solve for P and T
- In xRage we store an internal tabular EOS as a pressure/temperature table of density and internal energy
- Conceptually we could solve the 2X2 set of equations using Newton-Raphson

$$e = e(P,T),\ V = V(P,T)$$

$$e = e(P^n,T^n) + \frac{\partial e}{\partial P}(P^n,T^n)\left[P^{n+1} - P^n\right] + \frac{\partial e}{\partial T}(P^n,T^n)\left[T^{n+1} - T^n\right]$$

$$V = V(P^n,T^n) + \frac{\partial V}{\partial P}(P^n,T^n)\left[P^{n+1} - P^n\right] + \frac{\partial V}{\partial T}(P^n,T^n)\left[T^{n+1} - T^n\right]$$

- In practice this method doesn't work very well unless you have a starting point close to the desired solution
  - If the solution is inside or even close to a phase change this method likely will not converge at all
- In xRage we instead use a variation of a bisection/Newton scheme described on the next slide

PTE Solver, Bisection-Newton Method

- Michael Gittings, the originator of RAGE, invented this scheme
- Given a pressure P^n solve for the temperature on this isobar that yields the desired energy:

$$e = e\left(P^n, T^n\right)$$

  – Here we typically use a bisection method using the assumption that the derivative of energy with respect to temperature at constant pressure is non-negative
  – This is a stronger condition than thermodynamic stability since:

$$\left.\frac{\partial e}{\partial T}\right|_P = C_P - P\left.\frac{\partial V}{\partial T}\right|_P = C_V\left[1 + \frac{\Gamma}{c_T^2}\left(\Gamma C_V T - PV\right)\right],\ \Gamma = V\left.\frac{\partial P}{\partial e}\right|_V \text{, Grüneisen exponent, } C_P = T\left.\frac{\partial S}{\partial T}\right|_P = \text{ specific heat at constant pressure}$$

$$C_V = T\left.\frac{\partial S}{\partial T}\right|_V = \text{ specific heat at constant volume, } C_P \geq C_V \geq 0,\ c_T^2 = \left.\frac{\partial P}{\partial \rho}\right|_T \geq 0 = \text{ isothermal sound speed}$$

  – However this condition is usually satisfied by many if not most EOS models used in practice

- Do a Newton iteration to solve for specific volume along the iso-energy curve to get an updated value for the pressure:

$$P^{n+1} = P^n + \frac{\left(V - V^n\right)\left(\frac{\partial e}{\partial T}\right)^n}{\left(\frac{\partial V}{\partial P}\right)^n\left(\frac{\partial e}{\partial T}\right)^n - \left(\frac{\partial V}{\partial T}\right)^n\left(\frac{\partial e}{\partial P}\right)^n}$$

What can go wrong? (Almost Everything!)

- The EOS models used in practice:
  - May not be thermodynamically consistent (no underlying free energy)
  - May not be thermodynamically stable
  - Have limited domains of validity and stability and it is easy to go outside those domains
  - Material models can be stiff in specific volume (or other variables) so that small errors in the density produce huge changes in pressure and temperature
  - Have inaccurate Thermodynamic derivatives
    - Low order interpolation methods for tables may give poor results for numerical derivatives
    - High order interpolation methods may give noisy derivatives
  - Mixtures of materials with very different properties (gas and liquids for example) may not overlap in their domain at energies and densities produced by the hydro scheme
    - Metals for example can support tension (negative pressures) when you try to mix a metal with a gas that must have non-negative pressure you get trouble
  - Cavities and vacuums are problematic since few hydro codes are able to compute adiabatic expansions to low pressures consistently
    - Density and pressure do not go to zero at the appropriate rates to keep the sound speed finite
  - EOS evaluations are expensive
    - This is may seem odd to people who only work with perfect gases
    - Table evaluate requires a fast look-up algorithm
    - Mixed cell EOS evaluations require a system of multiple variables in multiple unknowns
    - Failure to converge happens more frequently than we would like
    - EOS evaluations often require the inversion of one form into another

What can go Wrong?

- Many algorithms would like to take advantage of the properties of entropy
  - Extract Riemann problem based methods
    - Mostly this is important to reduce discontinuous initial transients, once a wave profile is produced approximate or even linear Riemann problem solvers are sufficient
    - Ghost fluid extrapolation, an isentropic extrapolation is one of several schemes used to implement a ghost fluid method.
- For incomplete equations of state, isentropes are well defined but not the entropy
  - Solving for the entropy (or isentropes) on the fly is expensive even when it is well defined since it requires repeated solutions of non-trivial ordinary differential equations
- Example: Mie-Grüneisen EOS

$$P - P_r(V) = \frac{\Gamma(V)}{V}\left[E - E_r(V)\right]$$

$$TdS = dE + PdV = d\left[E - E_r(V)\right] + \frac{\Gamma(V)}{V}\left[E - E_r(V)\right]dV + \left[E_r'(V) + P_r(V)\right]dV$$

$$e^{\int\frac{\Gamma(V)}{V}dV}TdS = d\left[e^{\int\frac{\Gamma(V)}{V}dV}\left[E - E_r(V)\right] + \int e^{\int\frac{\Gamma(v)}{v}dv}\left[E_r'(V) + P_r(V)\right]dV\right] = d\xi$$

Isentropes are curves where ξ is constant

$$S = S(\xi),\ T = e^{-\int\frac{\Gamma(V)}{V}dV} / S'(\xi),\ C_V = -\frac{S'(\xi)^2}{S''(\xi)} \geq 0$$

Tension

- Tension is a state of negative pressure
- Typically occurs for metals and other solids
- Tension is a meta-stable state
  - It is in local thermodynamic equilibrium but not global equilibrium
    - Meta-stable states also can occur at vapor-liquid phase transitions
  - The global equilibrium has pressure equal to zero
- Tension can not PTE mix with a gas as the gas would be out of domain
- When mixing two metals in tension care needs to be taken that both are in domain
- In xRage we truncate the tension loop in specific-volume/temperature space at the minimum negative pressure
  - For specific volumes above this minimum we instantly relax to zero pressure
  - Effectively this means for the hydrodynamics to be well behaved we should stay well away from this minimum

General Out of Domain Mixtures

- When mixing different materials with separate EOS domains we will frequently encounter mixtures that have no overlap in domain where the given density and energy conditions can be satisfied
- Most commonly the specific internal energy for the mixture is too low
  - Occurs more than we could like for energy conserving codes that are kinetic energy dominated since the internal energy is recovered from the total energy by subtracting out the kinetic energy which is the same order of magnitude as the total energy
    - But of course energy conservation is needed to get shock jumps correct
    - Internal energy conservation (i.e. entropy conservation) yields rarefaction shocks
  - Effectively the internal energy becomes "noise"
- In xRage we punt by enforcing an internal energy minimum based the component EOS models
  - The internal energy computed by the difference between total and kinetic energy is floored by the mass average of the component internal energy minimums
  - During the PTE solver the component energies are floored at their domain minimums
  - This will often cause the solver to fail to converge so we normalize the final answer to ensure the volume average is at least correct even if we can not satisfy the energy average

Other Mixture Approaches

- There are many other ways to treat mixtures based on additional dynamic models for the components
- Generally these approaches do not yield a full set of conservation laws
- Component mass, total momentum, and total energy are conserved, but the additional equations may not be in conservation form

Single Pressure Mixtures

- Thermal isolation
  - This models assumes that all of the components in the mixture are in pressure equilibrium but not temperature equilibrium
  - Component entropies advect with the flow

$$T_k \frac{DS_k}{Dt} = \frac{De_k}{Dt} + P \frac{DV_k}{Dt} = 0$$

- Uniform strain/Uniform compression
  - This model assumes that all of the components experience the same proportional compression

$$\frac{1}{V_k} \frac{DV_k}{Dt} = \nabla \bullet \mathbf{u}$$

  - This equation is equivalent to the condition that the volume fractions of the components advect with the flow

Multiple Pressure Mixtures

- In this models the effective pressure is generally the volume average of the component pressures
  - Dalton mix is in this class since all the volume averages are equal to one
- Thermal isolation assumes the component entropies advect with the flow
- Uniform strain assumes the component volume averages advect with the flow
  - This is a common model for mixtures of metals with strength

Strength

- I won't provide details of how to model strength in a hydrocode, just point out a few EOS related issues
- Typically flows with strength are adjoined to the basic conservation laws as well as the mixture models described above
- It is common to use a hypo-elastic/plastic formulation that provides a dynamic equation for the deviatoric stress in terms of a shear modulus and velocity strain
  – No more detail, sorry this is a big topic in itself
- Front tracking is extremely beneficial here since the mixing of the constitutive properties of the strength laws is at best ad-hoc

Summary

- Treating flows with general equations of state is a tricky business, especially for mixtures
- It is important that the basic hydro scheme be aware of the EOS domain issues that arise when using more realistic equations of state
- Tabular methods for the EOS are powerful but care must be taken to handle interpolation off the table is a consistent manner
- Mixtures come in a variety of flavors and the choice of one model or another is going to be problem dependent.